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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to the Extraction of Phenols from Solution

We, THE GAS COUNCIL, a British body corporate, of 1 Grosvenor Place, London S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is for improvements in or relating to the extraction of phenols from solution and is particularly concerned with the extraction of phenols from aqueous solutions thereof.

It is known that natural clay minerals as well as certain synthetic materials resembling them are capable of entering into ion-exchange reaction with organic ccmpounds which contain functional groups capable of replacing inorganic cations in the mineral structure. It is also known that organic compounds which possess a centre of electrical dissymmetry, *i.e.* compounds which have a dipole moment, may be adsorbed by clay minerals. In such cases a stable organo-clay derivative may be formed.

We have now found that particular organo-clay derivatives have the property of extracting certain organic substances from solution in solvents which solvents are not themselves preferentially adsorbed by the organo constituent of the derivative. Thus, for example, such an organo-clay derivative prepared by reacting a primary aliphatic amine with bentonite is capable of extracting phenol from its solution in water.

We have further found that such organo-clay derivatives are particularly effective for the extraction of organic compounds whose molecules themselves contain a centre of electrical dissymmetry, and that the stronger is this effect, the more effective is the extraction of the substance from the solution. All phenols are adsorbed, particularly those compounds having unsymmetrically substituted molecules. Thus, for example, phenol and pyrocatechol are relatively strongly adsorbed.

According to the present invention there is provided a method of extracting phenols from solution, which method comprises bringing an organo-clay derivative into contact with the solution containing phenolic material whereby the phenolic material is adsorbed by the organo-constituent of the organo-clay derivative, the said organo-constuent being derived from a primary, secondary or tertiary amine or a quaternary ammonium compound and which organo-constituent contains at least 8 carbon atoms, and the solvent of the solution being one which is not itself preferentially adsorbed by the organo-clay derivative.

The solvent for the phenols is preferably water.

The organo-clay derivatives are preferably prepared from natural clays or clay minerals, of which the principal constituents are clay minerals with ion-exchange centres and expanding lattices, such as for example bentonite or other minerals containing montmorillonite. Organo-clay derivatives can be prepared from other minerals, particularly fine clay minerals described as livesite, or clay minerals which can act as adsorbents for example kaolinite but are less suitable than those having expanding lattices. The clay minerals are caused to combine with the organic base, which is preferably a long carbon chain molecule.

It is believed that when a straight chain primary amine is employed, the most satisfactory performance is obtained when the available internal and external surface of the clay mineral is between 50% and 90% covered with a coating of organic molecules. Generally, best performance is obtained

where with any given mineral and a particular amine or quaternary ammonium compound the maximum amount of organic base is combined which includes base-exchange and adsorption with the mineral, *e.g.* bentonite will combine with dodecylamine up to 18.2 per cent by weight on the weight of the derivative.

While saturated long chain organic bases adsorbed on clays are preferred for use in the method of the present invention, the carbon chains of the organic bases may be unsaturated and having a wide range of chain length. Such organo-clay derivatives are effective for the extraction of organic substances from solution, for example, straight chain aliphatic primary amines combined with a clay mineral are effective for the extraction of phenols from water, the efficiency of extraction first increasing with the number of carbon atoms in the chain to a maximum with dodecylamine. Preferably the number of carbon atoms in the chain is between 8 and 18. Subsequently, on further increasing the chain-length, the extractive power tends to decrease, but it may be found that primary amines of a greater chain length are more strongly retained than dodecylamine, good retention in any case being found with from 12 to 18 carbon atoms in the chain. It is found, for example, that octadecylamine, although its extractive power when adsorbed on a clay mineral is lower than that of dodecylamine, is nevertheless itself more strongly adsorbed on the mineral surface. This fact is of importance, for example, when the process is employed to extract phenols from industrial effluents in order to render them more easily disposable, as the more strongly adsorbed activating agent is less likely itself to create effluent disposal problems than is the less strongly adsorbed activating agent. In a cyclic process of adsorption and desorption retention is of great importance and in such a process dimethyl dioctadecyl ammonium clay derivative having an organo-content in the range of from 10 to 40 per cent by weight is preferred as it has good adsorbtion properties and the organo-constituent is strongly retained against wash-out, *e.g.* with sodium hydroxide solution.

While natural clay minerals are suitable as base materials, it is possible to employ synthetic alumina silica compounds resembling montmorillonite in structure and possessing ion-exchange properties.

Any method of bringing liquids into contact with solids may be used in carrying out the process of the present invention. Thus, for example, aggregates of the clay minerals may constitute the packing of columns or towers through which the solution to be treated is passed.

An alternative method, based on our further discovery that the formation of the organo-clay derivatives and the adsorption thereon of the phenol to be extracted may take place simultaneously, comprises the addition of an organic activating agent of the type described, *i.e.* a primary, a secondary or tertiary amine or a quarternary ammonium compound (the said amine or quarternary ammonium compound being one which contains at least 8 carbon atoms) to the solution to be treated, followed by bringing the solution into contact with the clay mineral.

Accordingly, the present invention also includes a modification of the method of extracting phenols from solution claimed in any one of the preceding claims wherein the formation of the organo-clay derivative and the adsorption thereon of the phenol to be extracted is effected by bringing a solution containing one or more phenols and a primary, secondary or tertiary amine or a quaternary ammonium compound (the said amine or quaternary ammonium compound being one which contains at least 8 carbon atoms) into contact with a clay mineral.

This latter method may be economically advantageous by comparison with the former, and may be preferred in particular when the organo-clay derivative, with its adsorbed phenol obtained from the solution, is itself a desired product. The former method, however, may effect a more complete removal of the phenol from the solution to be treated since an equilibrium is established at each point in the system between adsorbed phenol and dissolved phenol.

Recovery of the extracted phenolic compounds from the organo-clay derivative may be effected by direct treatment with steam. Alternatively, recovery of the extracted material may be effected by elution. Thus, for example, the recovery of the phenolic compounds may be effected by elution with solutions of caustic alkali.

Following is a description by way of example of methods of carrying the present invention into effect. Unless otherwise stated the methods described in the Examples were carried out at room temperature; the various organo-clay derivatives employed contained the maximum amount of organo constituent.

EXAMPLE 1

To 10 litres of a solution of phenol in water containing 101.4 grams of phenol was added 200 grams of hexadecylammonium bentonite containing 19.4% by weight of the organo constituent in the form of a 200 mesh powder. The organo-clay derivative was thoroughly dispersed in the phenol solution and the mixture was stirred for one hour. After this time it was found that equilibrium between the clay and the aqueous phase had been established and the amine-clay had adsorbed 18.4 grams of the phenol from solution. Untreated bentonite was found to adsorb no appreciable amount of phenol from

an aqueous solution under comparable conditions.

EXAMPLE 2

To 10 litres of a solution of *m*-cresol in water containing 9.08 grams of the cresol was added 54 grams of tetradecylamine (in form of its acetate salt). When the amine had dissolved 200 grams of natural bentonite was added and the mixture was thoroughly stirred until the bentonite had been completely dispersed. Analysis of the aqueous phase showed that the amount of cresol in the solution had been reduced to 3.55 grams.

EXAMPLE 3

To 10 litres of a solution of *p*-cresol in water containing 94.6 grams of *p*-cresol was added 200 grams of bentonite and 44.5 grams of dodecylamine (in the form of its acetate salt). After stirring until the clay and amine were completely dispersed, analysis showed that the clay had adsorbed 51 grams of the cresol.

EXAMPLE 4

The procedure of Example 3 was followed except that 10 litres of an aqueous solution of pyrocatechol containing 95.1 grams of pyrocatechol was used. In this case the amine clay adsorbed 22.5 grams of the dihydric phenol.

EXAMPLE 5

The procedure of Example 3 was followed except that 5 litres of an aqueous solution of resorcinol containing 37.6 grams of resorcinol was used. It was found that the amine clay adsorbed 3.2 grams of resorcinol.

EXAMPLE 6

To 10 litres of a solution of phenol in water containing 37.1 grams of phenol heated to 60°C. was added 51 grams of dodecylamine (in the form of the acetate salt) and 200 grams of natural bentonite. After the clay and amine had been completely dispersed analysis showed that the clay had adsorbed 8.4 grams of phenol.

EXAMPLE 7

260 grams of dimethyl dioctadecyl ammonium bentonite containing 34.4% by weight of organo constituent was allowed to come to equilibrium with 10 litres of an aqueous phenol solution containing 40 grams of phenol. Analysis showed the organo-clay derivative to have adsorbed 17.4 grams of phenol from solution.

EXAMPLE 8

280 grams of dimethyl dioctadecyl ammonium bentonite was well mixed with 10 litres of an aqueous *m*-cresol solution containing 21 grams of *m*-cresol. After the system had reached a state of equilibrium the organo-clay derivative was found to have adsorbed 16.1 of *m*-cresol.

EXAMPLE 9

To 10 litres of an aqueous resorcinol solution containing 10 grams of resorcinol, 280 grams of dimethyl dioctadecyl ammonium bentonite was added. After equilibrium had been reached the organo-clay derivative had adsorbed 5.1 grams of resorcinol.

EXAMPLE 10

300 grams of dimethyl dioctadecyl ammonium bentonite was left for 12 hours in contact with 10 litres of sodium hydroxide solution containing 800 grams of sodium hydroxide. The sodium hydroxide solution was then removed from the clay, and the clay washed with water until all traces of sodium hydroxide had been removed. The resulting clay was then dispersed in 10 litres of an aqueous phenol solution containing 40 grams of phenol. When equilibrium had been reached the organo-clay derivative was found to have adsorbed 16.5 grams of phenol.

EXAMPLE 11

280 grams of dimethyl dioctadecyl ammonium bentonite was dispersed in 10 litres of an aqueous solution containing 20 grams of phenol and 21 grams of *m*-cresol. At equilibrium analysis showed the organo-clay derivative to have adsorbed 48% of the total phenol content.

EXAMPLE 12

5 litres of 4% bentonite slurry and 5 litres of an aqueous phenol solution containing 94.4 grams of phenol were mixed with 164 grams of Ethomeen C/20 (this is a material supplied by Armour Chemical Industries Limited having a formula

$$R - N\begin{cases}(CH_2CH_2O)_xH\\(CH_2CH_2O)_yH\end{cases}$$

where x + = 10 and R is derived from the coca amines, and the average molecular weight of the material is 645, in the form of the acetate salt. (Ethomeen is a Registered Trade Mark.) After standing for 4 hours at 20°C. the organo-clay derivative was found to have adsorbed 34.6 grams of phenol.

EXAMPLE 13

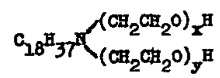
To a dispersion of 200 grams of bentonite in 5 litres of water was added 5 litres of an aqueous phenol solution containing 59.2 grams of phenol and 124 grams of Ethomeen T/15 (this is a material supplied by Armour Chemical Industries Limited having a formula

$$C_{16}H_{33}N\begin{cases}(CH_2CH_2O)_xH\\(CH_2CH_2O)_yH\end{cases}$$

where $x + y = 5$, in the form of the acetate salt. After equilibrium had been reached, the organo-clay derivative was found to have adsorbed 27 grams of phenol.

EXAMPLE 14

200 grams of bentonite were dispersed in 5 litres of water and mixed with 5 litres of an aqueous phenol solution containing 38.85 grams of phenol, and 181 grams of Ethomeen 18/20 (this is a material supplied by Armour Chemical Industries Limited having a formula



where $x + y = 10$, in the form of the acetate salt. When the system was in a state of equilibrium analysis showed the organo-clay derivative to have adsorbed 17.4 grams of phenol from solution.

EXAMPLE 15

202 grams of Fullers' Earth in 5 litres of water was mixed with 5 litres of water containing 40 grams of phenol and 147 grams of Ethomeen 18/20 in the form of the acetate salt. When equilibrium had been reached the organo-clay derivative was found to have adsorbed 16 grams of phenol.

EXAMPLE 16

368 grams of Fullers' Earth activated with Ethomeen 18/20, which had been previously dried at 100°C. was dispersed in 10 litres of an aqueous phenol solution containing 40 grams of phenol. After sufficient time had elapsed for the system to reach a state of equilibrium the organo-clay derivative was found to have adsorbed 17 grams of phenol.

EXAMPLE 17

The clay from Example 16 was separated from the phenol solution and washed with a solution of sodium hydroxide containing 40 grams of sodium hydroxide per litre of solution until no phenol remained adsorbed on the clay. It was then washed with water until all traces of sodium hydroxide had vanished and dispersed again in 10 litres of phenol solution containing 40 grams of phenol. At equilibrium the organo-clay derivative was found to have adsorbed 12.8 grams of phenol.

EXAMPLE 18

5 litres of vertical retort effluent was treated 4 times with 140 g. of dimethyl dioctadecyl ammonium bentanite. This reduced the oxygen adsorption (a measure of the phenolic content of the effluent) from 4000 to 200 and the resulting effluent was very pale yellow in colour.

EXAMPLE 19

100 grams of the dimethyl dioctadecyl ammonium bentonite or in later steps the regenerated dimethyl dioctadecyl ammonium bentonite were stirred with 6 litres of a solution of 1.5 mgm/gm phenol in water. The concentration of the phenol in the liquid phase was thus reduced to 0.5 mgm/gm. The filtered and washed clay was then stirred with 6 litres of a phenol solution of concentration 3 mgm/gm, when the concentration of the liquid phase was reduced to 1.5 mgm/gm. The filtered and washed clay was then stirred with 6 litres of phenol solution of concentration 4 mgm/gm when the phenol concentration was reduced to 3 mgm/gm. This represented a 3-stage counter-current batch process in which the overall phenol concentration was reduced from 4 mgm/gm to 0.5 mgm/gm. The clay was then contacted with a caustic-soda solution in two stages involving stirring, filtration and washing, whereby the greater part of the phenol was extracted, leaving a regenerated clay which could be returned to the process for a second cycle of operations. This process was carried out through the 5 cycles of 5-steps, at the end of which there was no detachable change in the adsorption capacity of the clay for phenol.

A further step of treating the effluent with the organo-clay derivative resulted in the concentration of phenol in the solution being reduced to between 0.1 and 0.2 mgm/gm.

EXAMPLE 20

The 5-step 5-cycle process as carried out in the preceding Example was repeated, using—instead of the synthetic phenol solution—an actual gas-works effluent containing phenols at a concentration of 4 mgm/gm when expressed on analysis as phenol. The result was the same as in Example 19 *i.e.* the phenol concentration was reduced to 0.5 mgm/gm and the adsorption capacity of the clay was unchanged. It was found desirable to remove gross insoluble impurities from the effluent before use, otherwise the effective life of the clay was reduced. These impurities were readily removed by a preliminary step of adsorption and filtration with a conventional material such as Kieselguhr, Fullers' Earth.

EXAMPLE 21

1% by weight of dimethyl dioctadecyl ammonium bentonite was added to a solution of cyclohexane containing 0.94% by weight of phenol. When equilibrium conditions had been established, it was found that 15% of the phenol was removed from the solution.

The experiment was repeated with a cyclohexane solution containing 0.47% by weight of phenol and when equilibrium conditions had been established, it was found that 36% by weight of the phenol originally present in the solution had been removed. The experiment was again repeated using cyclohexane solution containing 0.24% by weight of phenol. In this case it was found that 45% of the phenol present was removed by the organo-clay derivative, when equilibrium had been established.

WHAT WE CLAIM IS:—

1. A method of extracting phenols from solution, which method comprises bringing an organo-clay derivative into contact with

the solution containing phenolic material whereby the phenolic material is adsorbed by the organo-constituent of the organo-clay derivative, the said organo-constituent being derived from a primary, secondary or tertiary amine or a quarternary ammonium compound and which organo-constituent contains at least 8 carbon atoms, and the solvent of the solution being one which is not itself preferentially adsorbed by the organo-clay derivative.

2. A method as claimed in claim 1 wherein the solvent is water.

3. A method as claimed in any one of the preceding claims wherein the organo-clay derivative is prepared from a clay mineral, of which the principal constituents are clay minerals with ion-exchange centres and expanding lattices.

4. A method as claimed in claim 3 wherein the natural clays or clay minerals comprise bentonite or other minerals containing montmorillonite.

5. A method as claimed in any one of the preceding claims wherein the organo-constituent is a primary aliphatic amine having from 8 to 18 carbon atoms.

6. A method as claimed in any one of the preceding claims wherein the organo-clay derivative is prepared from bentonite and a salt of dimethyl dioctadecylamine.

7. A method as claimed in any one of the preceding claims wherein the solution from which one or more phenols are to be extracted is passed through one or more towers or columns packed with the organo-clay derivative.

8. A modification of the method of extracting phenols from solution claimed in any one of the preceding claims wherein the formation of the organo-clay derivative and the adsorption thereon of the phenol to be extracted is effected by bringing a solution containing one or more phenols and a primary, secondary or tertiary amine or a quaternary ammonium compound (the said amine or quaternary ammonium compound being one which contains at least 8 carbon atoms) into contact with a clay mineral.

9. A method of extracting phenols from solution substantially as hereinbefore described in any one of the specific examples.

10. An organo-clay derivative having adsorbed thereon one or more phenols when obtained by the method claimed in any one of the preceding claims.

11. Phenols when desorbed and recovered from the organo-clay derivative having a content of adsorbed phenol as claimed in claim 11.

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